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NACA RESEARCH MEMORANDUM

HEAT OF COMBUSTION OF THE PRODUCT FORMED BY THE REACTION OF DIBORANE WITH 1,3-BUTADIENE

By Stanley Tannenbaum and Harrison Allen, Jr.

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Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
WASHINGTON

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RESEARCH MEMORANDUM

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SUMMARY

The net heat of combustion of the product formed by the reaction of diborane with 1,3-butadiene was found to be 18,700 ± 150 Btu per pound for the reaction of liquid fuel to gaseous carbon dioxide, gaseous water, and solid boric oxide. The measurements were made in a Parr oxygen-bomb calorimeter, and the combustion was believed to be 98 percent complete. The estimated net heat of combustion for complete combustion would therefore be 19,075 ± 150 Btu per pound. Since this value is approximately the same as the heat of combustion of butadiene, it seems certain that the material is partially oxidized.

INTRODUCTION

At the request of the Bureau of Aeronautics, Department of the Navy, the NACA is participating in a project (Project Zip) aimed at the discovery and evaluation of certain high-energy fuels. The NACA will determine the fundamental flame velocity, heat of combustion, and possibly other combustion properties of fuel samples submitted by companies participating in the project as contractors to the Bureau of Aeronautics, Department of the Navy.

A sample of material formed by the reaction of diborane with 1,3-butadiene was received from the Mathieson Chemical Corp., and the heat of combustion of this material has been measured in a Parr oxygen-bomb calorimeter. Although the precision of the data is not equal to that obtained for hydrocarbons or for the alkylsilanes previously published by the NACA (refs. 1 and 2), this report was prepared at the NACA Lewis laboratory to make the data available as soon as possible.

TEST SPECIMEN

A sample of the product, which was obtained from the Mathieson Chemical Corp. in a sealed 50-milliliter flask, was stored at 0° C until ready for use. The analytical data of table I were also sent by the company. The nature of the material was unknown; however, it was stated that it was almost certainly an impure compound. The material was a yellow viscous fluid

containing a fine white precipitate that is now believed to be boric oxide or some intermediate oxidation product of boron. Tests in this laboratory indicated that it reacts rapidly in air and ignites spontaneously in an oxygen-enriched atmosphere. Fractions of the product were transferred in a helium-filled dry box into small glass bulbs, capped, and then sealed as quickly as possible. The quantity of liquid used in a run varied from 0.25 to 0.45 gram. The product seemed to become more viscous on standing and, consequently, more difficult to transfer into the glass bulbs.

APPARATUS AND PROCEDURE

The apparatus consisted of a Parr adiabatic calorimeter equipped with an Illium constant-volume bomb and a mercury thermometer that could be read to $\pm 0.005^{\circ}$ F. The bomb was calibrated with standard benzoic acid supplied by the Parr Instrument Company. The samples were introduced into small glass bulbs in a helium-flushed dry box by means of a hypodermic syringe. Enough liquid was introduced so that at room temperature the liquid occupied the entire volume. In order to make a determination, the bulb was attached to the iron ignition wire with a preweighed piece of cellulose tape, a perforated nickel crucible was placed around the bulb, and the bomb was filled with 25 atmospheres of oxygen. The heat generated by the burning of the wire and cellulose tape caused the liquid to rupture the glass bulb and burn.

In sealing-off the glass bulbs, a small amount of carbonization invariably resulted at the point where the seal was made. However, this did not involve any significant amount of material.

Attempts were also made to burn samples of the product in gelatin capsules. The capsules were weighed and filled with liquid in the dry box. They were then weighed again as quickly as possible and the seam was wrapped with a preweighed piece of cellulose tape which also served to attach the capsule to the ignition wire. Such samples warmed up slightly while they were being weighed and were apparently undergoing slow oxidation during this part of the handling procedure.

Carbon dioxide formed in the combustion was absorbed in Ascarite after the gas had been dried by passage through Anhydrone. When all the gas had been flushed out with fresh oxygen, the bomb was opened and examined for signs of incomplete combustion. It was then washed with distilled water and the washings were titrated to determine nitric acid formed by the oxidation of the atmospheric nitrogen during the combustion. The final step was to remove metals in solution with barium carbonate and titrate for boric acid (ref. 3) using a Fisher Titrimeter.

In order to check the carbon analysis obtained during the measurement of the heat of combustion, two separate analyses were made. The

samples, contained in glass bulbs, were placed in a special bomb which could be heated to high temperatures in order to give as complete oxidation as possible. The bomb was pressurized with 25 atmospheres of oxygen and heated to red heat for 1/2 hour. It was then cooled and the combustion gases were absorbed in Ascarite.

RESULTS AND DISCUSSION

Five determinations were made using the liquid-filled glass bulbs; the three most consistent runs are given in table II. The other two values are not included because a visual inspection of the bomb showed that the combustion was not sufficiently complete. The heats of combustion are the gross uncorrected values determined directly in the bomb with gaseous carbon dioxide, liquid water, and solid boric acid as the combustion products and with part of the boric acid dissolved in the water present in the bomb. This gross heating value is 19,887 ± 150 Btu per pound. The determined percent carbon, as carbon dioxide, was much above the Matheson value, whereas the percent boron was considerably below the stated value.

In order to convert the uncorrected gross value to a corrected net value, it was necessary to know the chemical composition of the product. The analysis obtained from the combustion process give a B/C ratio very close to 1/4. This is also the B/C ratio for tetraethyldiborane, which is formed by the reaction of diborane with ethylene. Although this does not prove that the Matheson product is impure tetraethyldiborane, it seems reasonable, in view of the lack of information regarding its composition, to consider it as such for the purposes of correcting the gross heating value obtained.

The first two corrections applied to the raw data are those used with tetraethyldiborane (ref. 4):

1. Conversion from a constant-volume process to a constant-pressure process, +4.1 kilocalories per mole.

2. Correction for the heat of hydration of boric oxide to boric acid and the heat of solution of part of the acid so formed, -16.0 kilocalories per mole (ref. 5).

Corrections 1 and 2 result in a value of 19,734 Btu per pound for the reaction

$$B_2C_8H_{22(l)} + 15\ O_{2(g)} \longrightarrow 8\ CO_{2(g)} + 11\ H_2O_{(l)} + B_2O_{3(s)}$$

A further correction is needed to yield the net heat of combustion.

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3. Correction for the latent heat of vaporization of the water formed during combustion, assuming the sample contains 11 percent hydrogen (table I), - 1028 Btu per pound.

Thus, the heat of combustion to gaseous water, gaseous carbon dioxide, and solid boric oxide becomes 18,706 ± 150 Btu per pound, which is rounded off to 18,700 ± 150 Btu per pound.

This value is considered to be somewhat lower than the actual heating value of the material for the following reasons: In all cases, small amounts of black material were found among the combustion products. This material was insoluble in hot nitric acid and is probably carbon. Also, in sealing-off samples in glass bulbs, some carbonization invariably resulted at the seal-off point.

To determine how large these errors might be, two types of experiments were performed in an effort to burn completely the carbon in a sample and compare this value with the carbon analysis obtained from the Parr bomb.

Several samples were burned in a heavy walled stainless-steel bomb which was filled with 25 atmospheres of oxygen and heated to red heat for 1/2 hour. The carbon dioxide formed was absorbed in Ascarite and gave the following results:

Run 1	percent carbon = 68.2
Run 2	percent carbon = 66.0

An effort was made to determine the heat of combustion of samples of the material sealed in gelatin capsules of known composition. Unfortunately, all such attempts gave ignition before the bomb could be placed in the calorimeter bath. In two experiments, the sample ignited spontaneously when only 5 or 6 atmospheres of oxygen were present in the bomb, which indicates that the material is spontaneously inflammable in an oxygen-enriched atmosphere. However, two samples did not explode until 25 atmospheres of oxygen had been introduced, and these samples seemed to burn to completion. Carbon and boron analyses were performed on the combustion products with the following results:

Run 1	percent carbon = 67.9 percent boron = 15.5
Run 2	percent carbon = 66.7 percent boron = 15.9

These data indicate that the heat of combustion reported represents approximately 98 percent combustion and, therefore, a more reasonable value would be 19,075 ± 150 Btu per pound.

The net heat of combustion of diborane is reported as 31,373 Btu per pound (ref. 6), and the gross value for liquid 1,3-butadiene is 20,047 Btu per pound (net value, 19,007 Btu/lb) (ref. 7). It is difficult to understand why the heating value for the reaction product of diborane with 1,3-butadiene is roughly the same as for butadiene alone, unless one assumes that the product had already become partially oxidized during its preparation. The presence of a white precipitate in the material when received lends support to this suggestion. If tank nitrogen was used without purification in the synthesis, the oxygen may have entered in this way; the Lewis laboratory has found that as much as 5 percent oxygen may be present in a given bottle when tank oil-pumped nitrogen is used.

The wide discrepancy in the analytical values given in tables I and II cannot be explained at this time.

Although the sample appeared to become more viscous on standing, its heating value did not change. In table II, experiments 1 and 2 were made on samples sealed-off immediately after opening the product tubes, whereas experiment 3 was made on a sample sealed-off after the product had remained in the helium-filled dry box at room temperature for 48 hours.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, August 5, 1953

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TABLE I. - ANALYSIS OF PRODUCT

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CHEMICAL CORP.

Constituent	Percent
Carbon	55
Boron	20
Hydrogen	11
Total	86

TABLE II. - HEAT-OF-COMBUSTION DATA FOR PRODUCT

OF REACTION OF DIBORANE AND 1,3 BUTADIENE

Experiment	Gross uncorrected heating values, Btu/lb	Analysis of combustion products	
		Carbon, percent	Boron, percent
1	19,915	66.4	15.7
2	19,746	65.7	15.4
3	20,000	67.2	15.4
Average value	19,887±150	66.4	15.5
Corrected net value	18,700±150		

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Fuels - Properties, Physical and Chemical 3.4.2

Combustion Research - General 3.5.1

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Abstract

The net heat of combustion of the product formed by the reaction of diborane with 1,3-butadiene was found to be 18,700 ± 150 Btu per pound for the reaction of liquid fuel to gaseous carbon dioxide, gaseous water, and solid boric oxide. The measurements were made in a Parr oxygen-bomb calorimeter, and the combustion was believed to be 98 percent complete. The estimated net heat of combustion for complete combustion would therefore be 19,075 ± 150 Btu per pound. Since this value is approximately the same as the heat of combustion of butadiene, it seems certain that the material is partially oxidized.